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AUTHOR(S):

Shigematsu, Tsunenobu; Tabushi, Masayuki

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Countercurrent Distribution of Iron and Copper in Acetylacetone-Butyl Acetate System

Tsunenobu SHIGEMATSU and Masayuki TABUSHI*

(Shigematsu Laboratory)

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Fundamental study on the countercurrent distribution was made on the ferric- and copper acetylacetonate system, using 1% acetylacetone-butyl acetate as an extracting solvent.

Distribution curves of the metals were obtained by twenty stages fundamental procedure at pH 2.0, 2.5, 3.0, 3.5 and 4.0. Experimental results showed a good agreement with theoretical values calculated by the binomial theorem from maximum position of the curves, and distribution ratios of ferric acetylacetonate derived from maximum position agreed with the values obtained from the batch extraction.

At pH 3, 3.5 and 4, the separation of ferric iron and copper was examined and the results were compared with the theoretical stage number necessary for the separation, which was given by an approximate equation with separation coefficient.

INTRODUCTION

Recently, solvent extraction is widely used as a powerful method for the separation of metals. Especially many chelating reagents such as 8-quinolinol, dithizone, cupferron, TTA *etc.* play important roles in the development of this technique. However, the usual single extraction procedure is not effective for the separation of materials which possess similar chemical property. The multi-stage extraction—countercurrent procedure—has been employed as a useful method in the separation of such substances as zirconium and hafnium¹⁾, rare earths²⁾, fission products or actinide elements³⁾, platinum group⁴⁾. *etc.* These were carried out mainly with an ion association system, such as TBP- or TBPO-mineral acid system.

The authors have studied on the solvent extraction and the separation of metal acetylacetonate, as previously reported⁵⁾, and now attempted to apply this chelating system to the countercurrent technique, for the purpose to develop acetylacetone extraction method.

In this paper, the fundamental problems—whether the experimental results agree with theoretical distribution curve or not, whether distribution ratios obtained from the curve agree with the value obtained from the batch extraction or not, whether actual experimental results agree with calculated stage number for complete separation or not, *etc.*—were examined, using ferric and copper acetylacetonate, of which the extraction behaviours were well known.

APPARATUS AND MATERIALS

A Mitamura's Semiautomatic Countercurrent Distribution Apparatus, Model

* 重松恒信, 田伏正之

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550-B, was used for the discontinuous multistage extraction. This apparatus based on the design of Craig⁶⁾ consists of one hundred distribution cells. A diagram of a unit cell is shown in Fig. 1.

Spectrophotometric, polarographic and pH measurements were made with a Hitachi's Photoelectric Spectrophotometer, Model EPU-2A, using 1cm silica cells, a Yanagimoto's Polarograph, Model PA-105, and a Hitachi-Horiba's pH Meter, M-3, respectively.

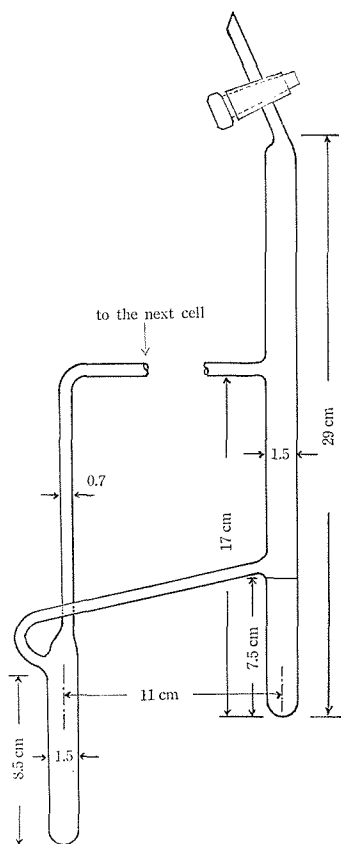


Fig. 1. Unit cell of countercurrent apparatus.

Ferric perchlorate solution, 100 μ g Fe/ml and 1.00 mg Fe/ml.

Copper sulphate solution, 1.00 mg Cu/ml and 5.00 mg Cu/ml.

1% Acetylacetone—butyl acetate solution.

5% Acetylacetone aqueous solution.

4M Ammonium chloride—4M ammonia solution.

EXPERIMENTAL RESULTS AND DISCUSSION

Twenty stages fundamental procedure was carried in this research, using 21 cells numbered 0, 1, 2,.....20 starting from the first tube, in which solvent was flowed. Distribution procedure was designed as follows:

Two hundred and fifty millilitres of water, whose pH is controlled to a

desired value, are shaken with 250 ml of 1% acetylacetone-butyl acetate. Aqueous solution is separated, after pH is adjusted again, transferred to the extraction apparatus, and every twenty tubes except the first one are filled up to the mark of 10 ml. One tenth to five tenth millilitres of iron or copper solution are diluted to 10 ml with the aqueous solution obtained above, and after pH adjustment injected to the first tube (cell No. 0). Then ten millilitres of extracting solvent treated as described above, are added to the first tube and shaken for 6~7 minutes (oscillation process). After the separation of two layers, upper organic layer of the first tube is transferred to the second one, and in the same time new 10 ml of extracting solvent to the first tube (transfer process). The similar processes of oscillation, separation and transfer are continued until first organic layer reaches to the last tube (cell No. 20). After the twenty first transfer process (therefore 20 times oscillation and separation process), iron and copper contained in every cells are determined by the following analytical procedures.

Ferric iron: In the case of iron, organic and aqueous layers were separately analysed in order to obtain distribution ratio in batch procedure. Acetylacetone method was applied in both cases. Namely, organic solution separated is directly used for the spectrophotometric determination by measuring absorbance at $440\text{ m}\mu$ against the extracting solvent⁷⁾. Aqueous layer is transferred to 50 ml beaker, and after 2 ml of 5% acetylacetone aqueous solution is added and pH is adjusted to 7, diluted to the mark in 20 ml volumetric flask. Absorbance is obtained at $440\text{ m}\mu$ against the reagent blank⁸⁾.

Copper: Copper was determined polarographically. Namely aqueous layer in each tube is transferred to 50 ml beaker and organic layer is washed with three portions of 5 ml of 2*N* hydrochloric acid. The stripping solutions are combined to aqueous layer of the same tube, and the resulting solution is evaporated to almost dryness. The residue is dissolved with small amount of water, and 5 ml of 4*M* ammonium chloride-4*M* ammonia solution and 0.5 ml of 2% gelatin solution are added. After diluted to 20 ml and deoxygenated with nitrogen gas, polarogram is recorded.

Distribution curves of ferric iron and copper at 11~12°C were shown in Fig. 2 and Fig. 3, using $250\text{ }\mu\text{g}$ iron and 1 mg copper, respectively. Open circles in figures represent experimental data, while points and curves, theoretical values which are calculated from maximum position by equation (1) and the binomial theorem, equation (2).

$$K = \frac{r_{\max} + 0.5}{20.5 - r_{\max}} \quad (1)$$

$$T_r = \frac{20!}{r!(20-r)!} \cdot \frac{K^r}{(K-1)^{20}} \quad (2)$$

where T_r is the fraction of substance present in the r -th tube, K , distribution ratio, and r_{\max} , maximum position of the distribution curve. As seen in figures experimental results are in good agreement with the calculated values.

On the distribution of iron, maximum position of the curves and distribution ratio calculated by equation (2) were compared with the values in batch

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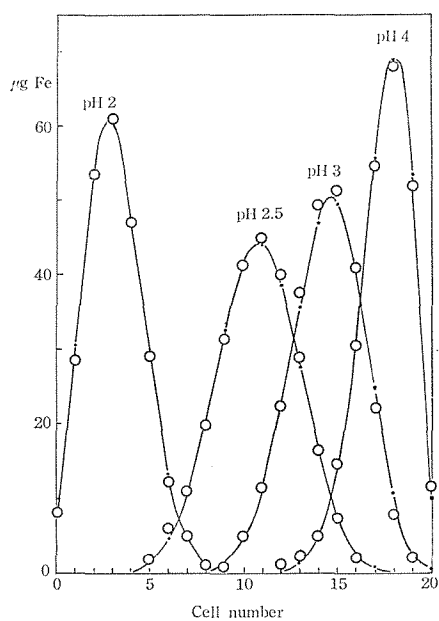


Fig. 2. Distribution curves of iron.

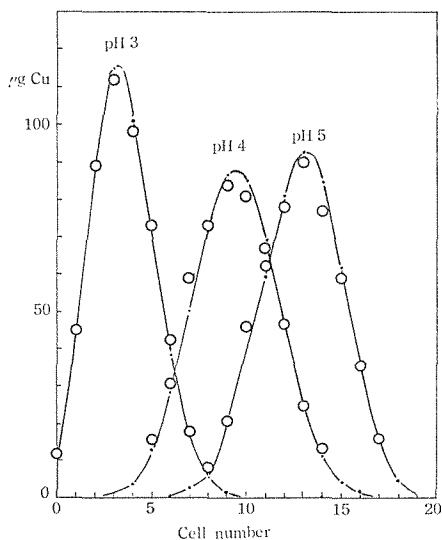


Fig. 3. Distribution curves of copper.

extraction. The latter distribution ratio, K' , is given by equation (3), and maximum position, r'_{\max} , is calculated by equation (4).

$$K' = \frac{\text{concentration of iron in (r+1)th organic layer}}{\text{concentration of iron in r-th aqueous layer}} \quad (3)$$

$$r'_{\max} = \frac{20.5 K' - 0.5}{1 + K'} \quad (4)$$

Results were shown in Table 1, of which the first column represented the values from distribution curves and the second, mean values of batch extraction. Both

Table 1.

pH	K	r _{max}	K'	r' _{max}
2.0	0.18 ₅	2.8	0.16 ₀ ^a	2.4 ₀
2.5	1.16 ₄	10.8	1.15 ₃ ^b	10.7 ₅
3.0	2.62 ₁	14.7	2.65 ₇ ^c	14.7 ₆

^a Average of 6 measurements $\sigma \pm 0.005$ ^b " of 7 measurements $\sigma \pm 0.02_6$ ^c " of 6 measurements $\sigma \pm 0.06_0$

distribution ratios and maximum position show good agreements.

Distribution curves with different amounts of iron or copper (100 μ g \sim 1 mg) under the same condition gave the same shape, although the figures were omitted. This fact indicates that acetylacetone extraction may be an ideal system.

On the basis of these results, the separation of iron and copper was examined. Table 2 showed the width of distribution curves and number of cells in which 99.7% of substance was contained. The width of the curves were calculated on an assumption that they were Gauss' normal distribution curve*. Table 2 reveals distribution at pH 3.0, 3.5 and 4.0 are suitable for the separation. Therefore volume factor**, α , separation coefficient***, β and the stage number necessary for the separation**** under these conditions were obtained. Table 3 shows that 99.7%

Table 2.

	pH	K	$4r_{99.7\%}$	Cell No.
Fe	2.0	0.19	9.8	0 - 8
"	2.5	1.16	13.4	4 - 18
"	3.0	2.62	12.0	8 - 20
"	3.5	3.88	10.8	10 - 20
"	4.0	7.40	8.7	14 - 20
Cu	3.0	0.21	10.3	0 - 9
"	3.5	0.34	11.7	0 - 11
"	4.0	0.89	15.0	1 - 17
"	5.0	1.84	12.8	6 - 20

Table 3.

pH	α	β	n _{99.7%}	n _{99%}	n _{95%}
3.0	0.55	12.5	19.9		
3.5	1.32	11.4	21.6	18.6	
4.0	6.59	8.3	27.7	23.8	16.6

$$* \quad 4r_{99.7\%} = 6\sqrt{20 \frac{K}{(1+K)^2}}$$

$$** \quad \alpha = K_{Fe} \cdot K_{Cu}$$

$$*** \quad \beta = K_{Fe}/K_{Cu}$$

**** It was given by an approximate equation, which was obtained by assuming volume factor unit:

$$n = \frac{C_R}{\frac{\beta+1}{\sqrt{\beta}}} - 2$$

where C_R was purity constant, and 36 for 99.7%, 31 for 99.0% and 21.6 for 95% purity.

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of iron and copper can be separated at pH 3.0; 99%, at pH 3.5; and 95%, at pH 4.0.

Distribution curves of the samples, containing 250 μg iron and 500 μg copper; were shown in Fig. 4, Fig. 5 and Fig. 6. Recoveries and contaminations of iron and copper are as follows:

	Cell No.	Fe	Cu
pH 3	0 - 8	0.3%	99. %
	10 - 20	99.	0.5
	11 - 20	97.	<0.2
pH 3.5	0 - 9	<0.2	98.
	0 - 10	1.	98.
	11 - 20	99.	1.
	12 - 20	97.	<0.2
pH 4	4 - 12	0.3	94.
	4 - 13	2.	98.
	14 - 20	98.	2.
	15 - 20	96.	0.5
	16 - 20	90.	<0.2

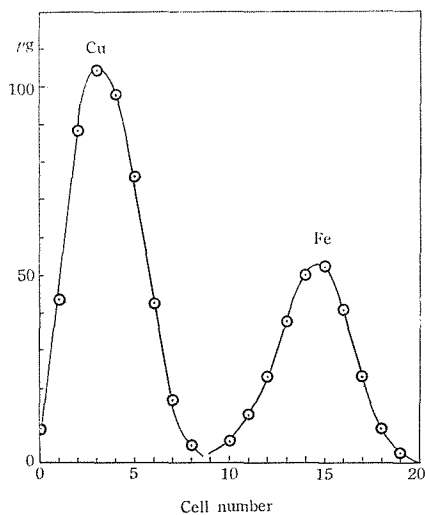


Fig. 4. Distribution of iron and copper at pH 3.0.

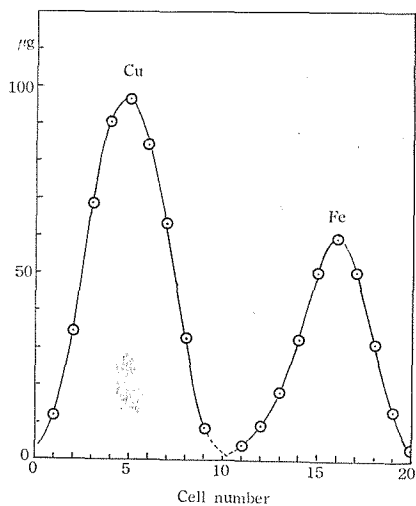


Fig. 5. Distribution of iron and copper at pH 3.5.

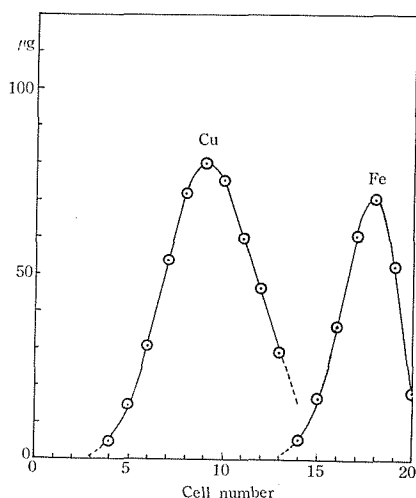


Fig. 6. Distribution of iron and copper at pH 4.0.

These results are somewhat worse than the values above calculated. It may be due to the fact that the theoretical values are derived from the approximate calculation.

The purpose of this investigation is a fundamental survey on the counter-current extraction using acetylacetone as a reagent. In the further research, the authors will study on the separation of the materials of which the separation can not be done by the single extraction process.

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